BREAKDOWN OF THE FRANCK-CONDON APPROXIMATION IN N_2

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INTRODUCTION

When a molecular electron is excited or ionized, it moves in a different charge distribution exerting in turn a different force on the nuclei. The nuclei respond by breaking into stronger vibrations. Electronic transitions are accompanied by vibrational transitions, which are called vibronic. The determination of which vibrations are stimulated is based on the view that nuclei move much faster than electrons, and so the rearrangement occurs in a virtually static nuclear frame. The Franck-Condon principle is the approximation that the nuclear conformation readjusts after the electronic transition, and not during it. The most probable conformation of the molecule when the transition begins is at the nuclei equilibrium position. At the end of the transition, the nuclei are still in their original position and this is the origin of the term vertical transition. The intensity of a transition between vibronic states depends on the magnitude of the transition moment. In the frame of the Franck-Condon approximation, it can be written as:

$$<\varepsilon'\nu'|\mu|\varepsilon\nu> = \mu_{\varepsilon'\varepsilon} * S_{\nu\nu'}$$

$S_{\nu\nu'}$ is the so-called Franck-Condon factor. It can then be seen that the ratio between two vibrational levels in the same electronic band should be constant.

Vibrational level intensity ratios as a function of photon energy have been determined in the valence spectrum of N_2 from 20-400 eV using photoelectron spectroscopy. Results for the B state show a large deviation from the Franck-Condon approximation and qualitatively agree with some recent fluorescent results [1,2].

EXPERIMENT

The experiment was conducted on beamline 10.0.1 at the ALS using a Scienta SES-200 hemispherical analyzer. The transmission function of the spectrometer was accounted for before extracting the gaussian fits of the peaks areas.

RESULTS

Vibrationally resolved photoelectron cross-sections of simple molecules were obtained close to threshold to explore the dynamical effects of shape resonances and Cooper minima on photoionization cross sections using 2nd generation light sources. Experimental resolution limitations made it impossible to extend those measurements beyond 40 eV. Recently, however, a recent experiment [1,2] was carried out to access vibrationally resolved photoionization data over a much wider spectral range using dispersed fluorescence from the residual photoion. Vibrational level population distributions of N_2^+ photoions in the $B^2\Sigma_u^+$ electronic state were probed by detecting the fluorescence emitted as they decayed into the $X^2\Sigma_g^+$ ionic state. Results for the B state shows a large deviation from the Franck-Condon approximation. We report in this work a *direct* similar study of this effect using photoelectron spectroscopy of these vibrational

levels population was conducted in the present experiment. Vibrational level intensity ratios as a function of photon energy were determined from 20-400 eV and are displayed in Fig.1 for the X state, in Fig.2 for the A state and in Fig.3 for the B state. Results for the B state show a large deviation from the Franck-Condon approximation consistent with the fluorescent results.

A complete analysis of the results is currently underway.

REFERENCES

[1] Rao et al, Phys. Rev. Lett. **76**, 2666 (1996).
[2] Prof. E. Poliakoff (private communication).

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Fig. 1 Branching ratio v_1/v_0 for the X state as a function of photon energy.

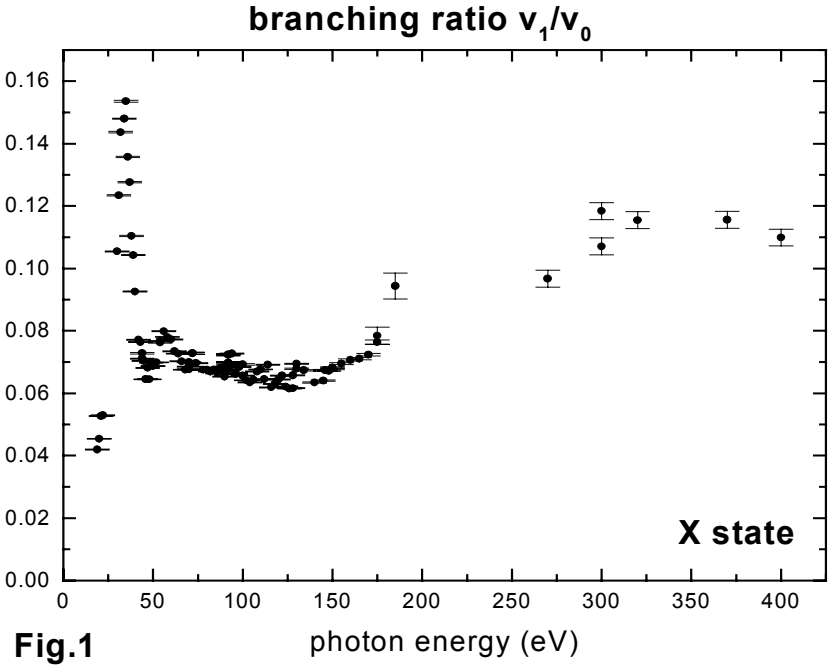

Fig.1

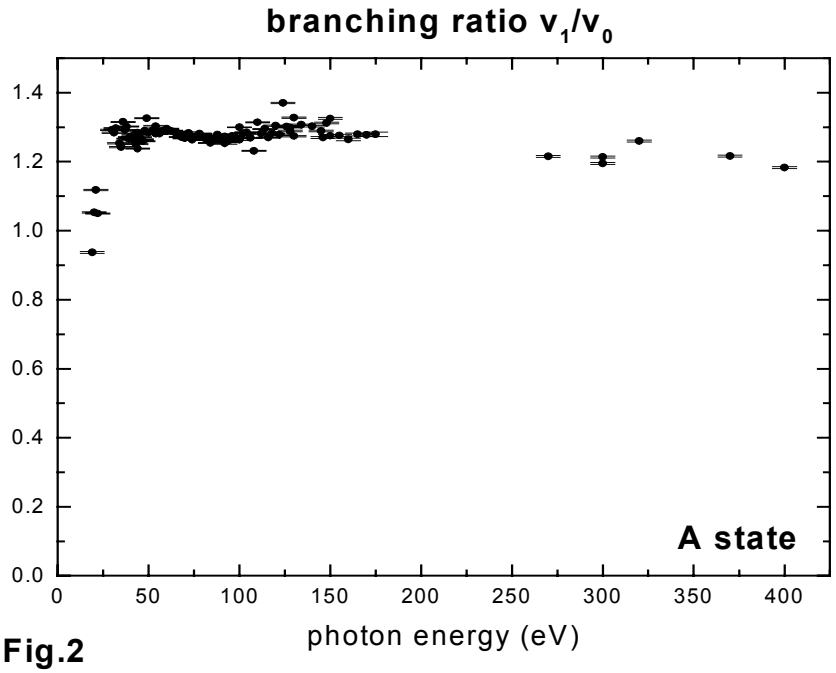

Fig.2 Branching ratio v_1/v_0 for the A state as a function of photon energy.

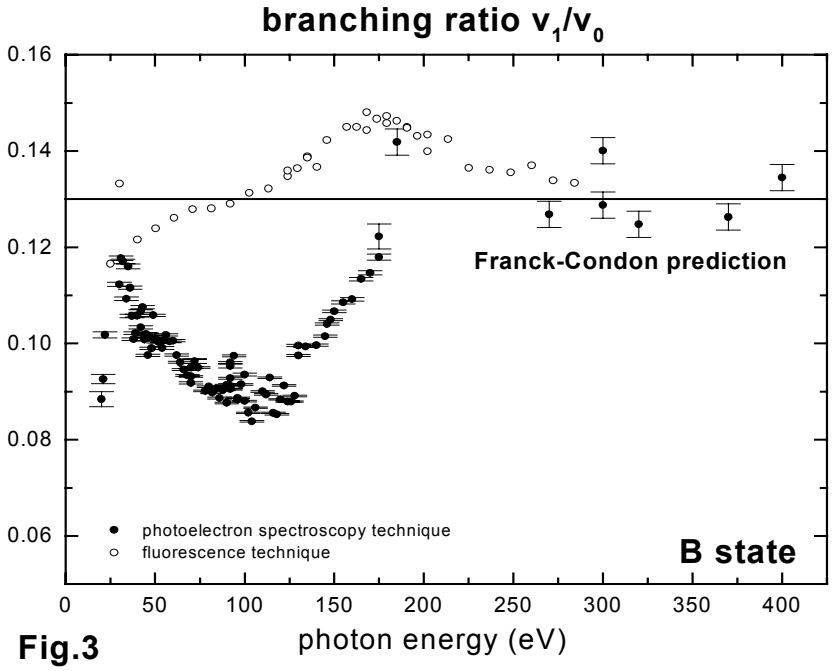

Fig.3 Branching ratio v_1/v_0 for the B state as a function of photon energy compared with fluorescence data (open circles).